

The University of Chicago

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BROMINE FROM ELECTRON SCATTERING

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

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WILLIAM E. FRYE

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A Determination of the Atomic Field of Bromine from Electron Scattering

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The experimental curves for the scattering of electrons by bromine have been analyzed to determine the phase shifts as functions of the energy. The method of phase shift analysis is described in detail. The atomic field of bromine is calculated from the phase shifts by a method involving the WKB approximation to the phase shifts.

THE angular distribution of electrons elastically scattered in bromine gas has been determined experimentally for several energies by Arnot.¹ Various attempts have been made to fit these experimental curves by calculation of the scattering intensity with phase shifts derived either from an estimate of the atomic field of bromine² for which the Hartree field has not yet been calculated, or by extrapolation of the phase shifts for the neighboring atom, krypton.³

In the present paper the above procedure is reversed. The experimental scattering curves are analyzed by a method developed by Voss⁴ to determine the phase shifts. The atomic field of bromine is then calculated from these empirical phases by an approximate method due to Hoyt and Frye.⁵

A finite number n of the phase shifts are assumed to be of importance, then the best approximation to the scattering intensity is obtained if

$$\int_{-1}^{+1} \left[I(\theta) - \frac{C}{4k^2} \sum_{l=0}^n (2l+1)(\exp 2iK_l - 1)P_l(\cos\theta) \right]^2 dx = \text{minimum}, \quad (2)$$

where $x = \cos \theta$. The measured intensity $I(\theta)$ can be expanded in a series of zonal harmonics,

$$I(\theta) = \sum_{\nu} B_{\nu} P_{\nu}(\cos\theta), \quad (3)$$

where the B_{ν} are constant coefficients which can be calculated from $I(\theta)$ by a method due to Gauss.⁶ We, using the formula for the expansion of the product of two zonal harmonics,⁷ can also

¹ F. L. Arnot, Proc. Roy. Soc. **A144**, 360 (1934).
² F. L. Arnot and J. C. McLauchlan, Proc. Roy. Soc. **A146**, 662 (1934).
³ C. H. Shaw and T. M. Snyder, Phys. Rev. **58**, 600 (1940).

⁴ W. Voss, Zeits. f. Physik **83**, 581 (1933).

⁵ F. C. Hoyt and W. E. Frye, Phys. Rev. **58**, 784 (1940).

⁶ E. W. Hobson, *Theory of Spherical and Ellipsoidal Harmonics* (Cambridge, 1931), p. 81.

⁷ Reference 6, p. 86.

PHASE SHIFT ANALYSIS BY THE METHOD OF VOSS

A brief account of the method of Voss⁴ is given below. The intensity of scattering (cross section per unit solid angle) can be represented in terms of phase shifts K_l , that are functions only of the energy of the incident electrons, by the familiar expression

$$I(\theta) = \frac{C}{4k^2} \left| \sum_{l=0}^{\infty} (2l+1)(\exp 2iK_l - 1)P_l(\cos\theta) \right|^2, \quad (1)$$

where k is the de Broglie wave number of the electrons, and a constant C , which is independent of the energy, has been included because only measurements of relative intensities are available. Given $I(\theta)$, one cannot calculate directly the phase shifts from Eq. (1). However, if only a

finite number n of the phase shifts are assumed to be of importance, then the best approximation

write

$$\begin{aligned} & \frac{C}{4k^2} \left| \sum_{l=0}^n (2l+1)(\exp 2iK_l - 1)P_l(\cos\theta) \right|^2 \\ &= \sum_{\lambda=0}^{2n} A_{\lambda}(K_0, K_1, \dots, K_n; C)P_{\lambda}(\cos\theta). \end{aligned} \quad (4)$$

The substitution of Eqs. (3) and (4) into Eq. (2) and the use of the orthogonality and normalization properties of the $P_l(\cos\theta)$ give the condition

$$\sum_{\nu=0}^{2n} \frac{(B_{\nu} - A_{\nu})^2}{2\nu+1} = \text{minimum}.$$

If the constant C is assumed to be known, this condition can be expressed in the form of the

system of equations,

$$\sum_{\nu=0}^{2n} \frac{B_{\nu}}{2\nu+1} \frac{\partial A_{\nu}}{\partial K_l} = \sum_{\nu=0}^{2n} \frac{A_{\nu}}{2\nu+1} \frac{\partial A_{\nu}}{\partial K_l}, \quad l=0, 1, \dots, n. \quad (5)$$

Adding $\sum_{\nu=0}^{2n} -(A_{\nu}^0/2\nu+1)(\partial A_{\nu}/\partial K_l)$ to both sides of each of Eqs. (5), where

$$A_{\nu}^0 = A_{\nu}(K_0^0, K_1^0, \dots, K_n^0),$$

and the K_l^0 are zero order approximations to the phase shifts, replacing $\partial A_{\nu}/\partial K_l$ by $\partial A_{\nu}^0/\partial K_l^0$ and expanding $(A_{\nu} - A_{\nu}^0)$ in a Taylor's series keeping only first-order terms one obtains

$$\sum_{\lambda=0}^n \Delta_{\lambda} C_{\lambda l} = C_l, \quad l=0, 1, \dots, n, \quad (6)$$

where

$$\Delta_{\lambda} = K_{\lambda} - K_{\lambda}^0,$$

$$C_{\lambda l} = C_{\lambda l} = \sum_{\nu=0}^{2n} \frac{1}{2\nu+1} \frac{\partial A_{\nu}^0}{\partial K_{\lambda}^0} \frac{\partial A_{\nu}^0}{\partial K_l^0},$$

$$C_l = \sum_{\nu=0}^{2n} \frac{B_{\nu} - A_{\nu}^0}{2\nu+1} \frac{\partial A_{\nu}^0}{\partial K_l^0}.$$

Equations (6) form a system of linear equations to be solved for the corrections Δ_{λ} to the phase shifts K_l .

The procedure can be repeated as many times as desired, in each case the A_{ν}^0 and $\partial A_{\nu}^0/\partial K_l^0$ calculated from the phase shifts obtained from the previous application of the method is used. The corrections in general become successively smaller so that satisfactory convergence is usually obtained after four or five applications of the method.

FIG. 1. Phase shifts for bromine deduced from the observed scattering of electrons.

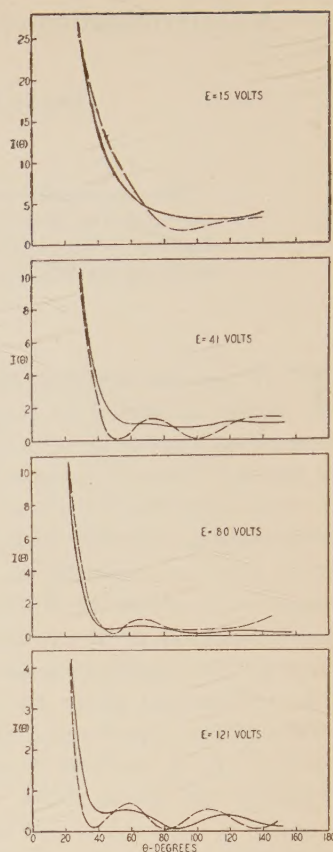
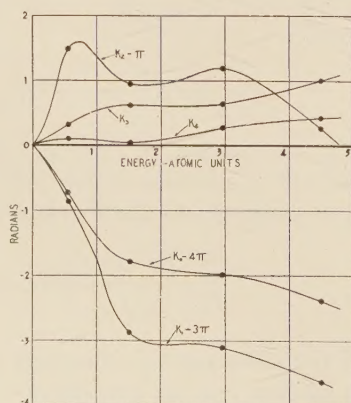


FIG. 2. Broken curves represent intensity against scattering angle θ calculated from the phase shifts of Fig. 1. Solid curves represent the experimental data of Arnot. All intensities are measured in atomic units.

The constant C can be included as an additional unknown in the above procedure, and an additional equation obtained in (6). Since C is independent of the energy, it need be determined only at one value of the energy. Calculation of C at the two energies, 15 ev and 41 ev, showed good agreement.

Phase shifts for bromine up to order five inclusive were calculated by the above method of Voss, with the phase shifts of Shaw and Snyder³ as zeroth-order approximations. It was found that from four to six successive applications of the method were required to reduce the corrections Δ_{λ} below 0.2 radian. The calculated phase shifts are shown in Fig. 1 where the phase shifts in radians are plotted against energy in Hartree atomic units. K_5 is not included because it was very small and varied irregularly about zero.

In Fig. 2 the scattering intensities in atomic units, calculated from the phase shifts of Fig. 1, are plotted in broken lines for the four energies, 15, 41, 80 and 121 ev. The experimental curves of Arnot, with the scattering intensities reduced to

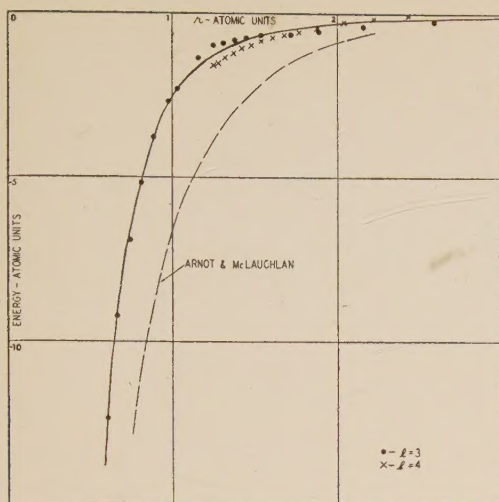


FIG. 3. The solid line represents the atomic field deduced from the observed scattering of electrons by bromine. Points are calculated from the phase shifts K_3 and K_4 of Fig. 1. For $l < 3$ the barrier is not removed, and the method of calculation is not applicable. The broken curve is the field extrapolated by Arnot and McLauchlan from the Hartree field of krypton.

atomic units by use of the calculated value of the constant C of Eq. (1) ($C=19.48$), are shown in solid lines. The high value of K_2 at 15 volts (15 eV = 0.55 atomic units of energy) seems to have physical significance, for a lower value gives poorer agreement of the scattering intensity with the experimental values.

DETERMINATION OF THE FIELD FROM THE PHASE SHIFTS

The potential field has been calculated directly from the phase shifts by a method⁵ involving the WKB approximation to the phase shifts. The method is applicable only if the effective field (actual field plus centrifugal term) contains no barrier. Calculation of points for the field of bromine, in which were used the phase shifts of order less than three, gave anomalous results, which were interpreted as due to the presence of a barrier in the effective potential for these low angular momenta. Points calculated from third- and fourth-order phase shifts (the barrier is removed for $l \geq 3$) are shown in Fig. 3, where the potential in atomic units of energy is plotted against radial distance in atomic units. The broken curve represents the field estimated by Arnot and McLauchlan² by extrapolation from the Hartree field of krypton.

Points obtained from phase shifts of one order are calculated quite independently of those from another order. The points in Fig. 3 which are derived from K_3 show good agreement with those from K_4 , and both sets of points lie on a smooth curve.

The calculated field in Fig. 3 is that field which acts on an electron at a distance r from the center of the atom, and hence it includes the polarization energy of the scattering atom due to the presence of the scattered electron. A discussion of this polarization correction has been given by Shaw and Snyder.³

DISCUSSION

Several limitations and sources of error have influenced the calculations here described. The scattering has been measured experimentally for only a few energies and over a limited angular range. Such factors as finite resolving power, space charge, etc., may have given rise to experimental errors. The methods of phase shift analysis and calculation of the field from the phase shifts are approximate in nature. Only a finite number of phase shifts have been assumed to be of importance. This assumption is valid for low energies, but higher order phase shifts may become important at higher energies. The distortion of the field due to the binding of the bromine atoms in the molecule has been neglected but may be expected to be small. Exchange effects, which may be important at low energies, have not been considered.

An attempt was made to calculate the fine structure of the x-ray absorption edge for bromine⁸ with the phase shifts calculated here. However, it was found that the shape of the curve was very sensitive to small variations in the lower order phase shifts at low energies, and good agreement with experiment was not obtained in that region. At higher energies somewhat better agreement than that of Snyder and Shaw was found.

The author wishes to express his deep appreciation to Professor Hoyt who suggested the problem and under whose guidance the calculations were carried out.

⁸ T. M. Snyder and C. H. Shaw, Phys. Rev. **57**, 881 (1940).



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